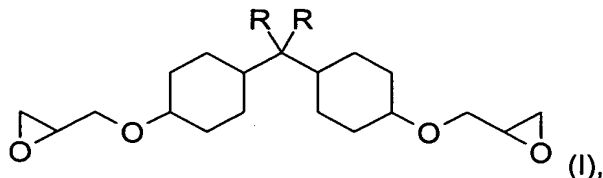


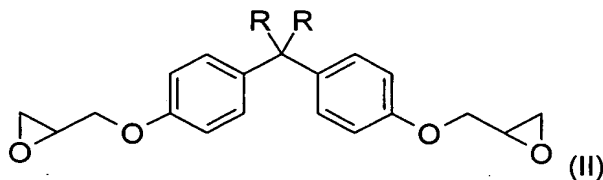
Heterogeneous ruthenium catalyst, nucleus-hydrogenated diglycidyl ether of bisphenols A and F, and method for the production thereof

# Description

The present invention relates to a heterogeneous ruthenium catalyst comprising silicon dioxide as support material, to a process for preparing a bisglycidyl ether of the formula I



where R is CH<sub>3</sub> or H, by ring hydrogenation of the corresponding aromatic bisglycidyl ether of the formula II



in the presence of a catalyst, and to bisglycidyl ethers of the formula I which can be prepared with this process.

The compound II in which R = H is also referred to as bis[glycidyoxyphenyl]methane (molecular weight: 312 g/mol).

The compound II in which R = CH<sub>3</sub> is also referred to as 2,2-bis[p-glycidyoxyphenyl]propane (molecular weight: 340 g/mol).

The preparation of cycloaliphatic oxirane compounds I which contain no aromatic groups is of particular interest for the production of light- and weathering-resistant surface coating systems. Such compounds can in principle be prepared by hydrogenation of the corresponding aromatic compounds II. The compounds I are therefore also referred to as "ring-hydrogenated bisglycidyl ethers of bisphenols A and F".

The compounds II have long been known as constituents of surface coating systems (cf. J.W. Muskopf et al. "Epoxy Resins" in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition on CD-ROM).

However, the high reactivity of the oxirane groups in the catalytic hydrogenation presents a problem. Under the reaction conditions usually required for the hydrogenation of the aromatic ring, these groups are frequently reduced to alcohols. For this reason, the hydrogenation of the compounds II has to be carried out under  
5 very mild conditions. However, this naturally results in a slowing of the desired aromatic hydrogenation.

US-A-3,336,241 (Shell Oil Comp.) teaches the preparation of cycloaliphatic compounds containing epoxy groups by hydrogenation of corresponding aromatic epoxy  
10 compounds using rhodium and ruthenium catalysts. The activity of the catalysts decreases so much after one hydrogenation that the catalyst has to be changed after each hydrogenation in an industrial process. In addition, the selectivity of the catalysts described there leaves something to be desired.

15 DE-A-36 29 632 and DE-A-39 19 228 (both BASF AG) teach the selective hydrogenation of the aromatic parts of the molecule of bis[glycidyoxyphenyl]methane or of 2,2-bis[p-glycidyoxyphenyl]propane over ruthenium oxide hydrate. This improves the selectivity of the hydrogenation in respect of the aromatic groups to be hydrogenated. However, according to these teachings too, it is advisable to regenerate  
20 the catalyst after each hydrogenation, with the separation of the catalyst from the reaction mixture proving to present problems.

EP-A-678 512 (BASF AG) teaches the selective hydrogenation of the aromatic parts of the molecule of aromatic compounds containing oxirane groups over ruthenium  
25 catalysts, preferably ruthenium oxide hydrate, in the presence of from 0.2 to 10% by weight of water, based on the reaction mixture. Although the presence of water makes the separation of the catalyst from the reaction mixture easier, it does not alleviate the other disadvantages of these catalysts, e.g. an operating life which is in need of improvement.

30 EP-A-921 141 and EP-A1-1 270 633 (both Mitsubishi Chem. Corp.) concern the selective hydrogenation of double bonds in particular epoxy compounds in the presence of Rh and/or Ru catalysts having a particular surface area or in the presence of catalysts comprising metals of the platinum group.

35 JP-A-2002 226380 (Dainippon) discloses the ring hydrogenation of aromatic epoxy compounds in the presence of supported Ru catalysts and a carboxylic ester as solvent.

40 JP-A2-2001 261666 (Maruzen Petrochem.) relates to a process for the continuous ring hydrogenation of aromatic epoxide compounds in the presence of Ru catalysts which are preferably supported on activated carbon or aluminum oxide.

An article by Y. Hara et al. in Chem. Lett. 2002, pages 1116ff, relates to the "Selective Hydrogenation of Aromatic Compounds Containing Epoxy Group over Rh/Graphite".

- 5 Tetrahedron Lett. 36, 6, pages 885-88, describes the stereoselective ring hydrogenation of substituted aromatics using colloidal Ru.

JP 10-204002 (Dainippon) relates to the use of specific Ru catalysts, in particular Ru catalysts doped with alkali metal, in ring hydrogenation processes.

- 10 JP-A-2002 249488 (Mitsubishi) teaches hydrogenation processes in which a supported noble metal catalyst having a chlorine content below 1500 ppm is used.

- 15 WO-A1-03/103 830 and WO-A1-04/009 526 (both Oxeno) relate to the hydrogenation of aromatic compounds, in particular the preparation of alicyclic polycarboxylic acids or esters thereof by ring hydrogenation of the corresponding aromatic polycarboxylic acids or esters thereof, and also to catalysts suitable for this purpose.

- 20 The processes of the prior art have the disadvantage that the catalysts used have only short operating lives and generally have to be regenerated in a costly fashion after each hydrogenation. The activity of the catalysts also leaves something to be desired, so that only low space-time yields, based on the catalyst used, are obtained under the reaction conditions required for a selective hydrogenation. However, this is not economically justifiable in view of the high cost of ruthenium and thus of the catalyst.

- 25 WO-A2-02/100 538 (BASF AG) describes a process for preparing particular cycloaliphatic compounds which have side chains containing epoxide groups by heterogeneously catalytic hydrogenation of a corresponding compound which contains at least one carbocyclic, aromatic group and at least one side chain containing at least one epoxide group over a ruthenium catalyst.

30

The ruthenium catalyst is obtainable by

- 35 i) treating a support material based on amorphous silicon dioxide one or more times with a halogen-free aqueous solution of a low molecular weight ruthenium compound and subsequently drying the treated support material at a temperature below 200°C,
- ii) reducing the solid obtained in i) by means of hydrogen at a temperature in the range from 100 to 350°C,
- 40 with step ii) being carried out immediately after step i).

WO-A2-02/100 538 discloses nothing about the ratio of the  $Q_2$  and  $Q_3$  structures  $Q_2/Q_3$  in the silicon dioxide.

5 The preferred catalysts A and B described in the examples (page 13) have a percentage ratio of the signal intensities of the  $Q_2$  and  $Q_3$  structures  $Q_2/Q_3$  in the silicon dioxide determined by means of solid-state  $^{29}\text{Si}$ -NMR of 30.

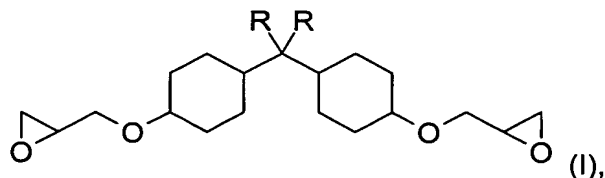
Furthermore, the silicon dioxide comprises Al(III) and Fe(II and/or III) in a concentration of 400 ppm by weight and alkaline earth metal cations ( $M^{2+}$ ) in a weight ratio of (Ca(II) + Mg(II)) : (Al(III) + Fe(II and/or III)) = 0.1. (cf. below).

WO-A2-02/100 538 teaches that the compounds used can "be either monomeric compounds or oligomeric or polymeric compounds" (page 9 above).

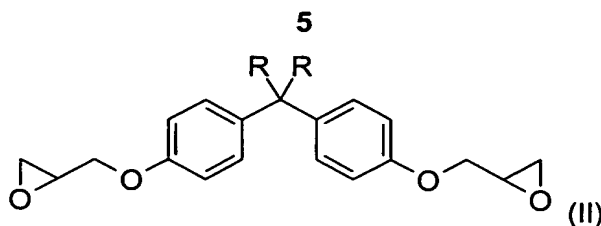
15 The Roman numbers in brackets after the element symbol indicate the oxidation state of the element.

It was an object of the present invention to provide an improved selective process for the hydrogenation of aromatic compounds II to the "ring-hydrogenated" compounds I, by means of which high yields and space-time yields [amount of product/(catalyst volume • time)] ( $\text{kg}/(\text{l}_{\text{cat}} \cdot \text{h})$ ), [amount of product / (reactor volume • time)] ( $\text{kg}/(\text{l}_{\text{reactor}} \cdot \text{h})$ ), based on the catalyst used, can be achieved and in which the catalysts used can be used for hydrogenations a number of times without work-up. In particular, catalyst operating lives which are higher than those obtained using the process according to WO-A2-02/100 538 should be achieved. Furthermore, bisglycidyl ethers of the formula I having improved properties, in particular in their typical applications, are to be found.

We have accordingly found a heterogeneous ruthenium catalyst comprising silicon dioxide as support material, wherein the percentage ratio of the signal intensities of the  $Q_2$  and  $Q_3$  structures  $Q_2/Q_3$  in the silicon dioxide determined by means of solid-state  $^{29}\text{Si}$ -NMR is less than 25, a process for preparing the bisglycidyl ether of the formula I



where R is  $\text{CH}_3$  or H, by ring hydrogenation of the corresponding aromatic bisglycidyl ether of the formula II



wherein the abovementioned heterogeneous ruthenium catalyst is used, and a  
 5 bisglycidyl ether of the formula I which can be prepared using the abovementioned  
 process.

An important constituent of the catalysts of the invention is the support material based  
 on amorphous silicon dioxide. In this context, the term "amorphous" means that the  
 10 proportion of crystalline silicon dioxide phases in the support material is less than 10%  
 by weight. However, the support materials used for producing the catalysts can display  
 superstructures formed by a regular arrangement of pores in the support material.

It is critical that the percentage ratio of the  $Q_2$  and  $Q_3$  structures  $Q_2/Q_3$  determined by  
 means of solid-state  $^{29}\text{Si}$ -NMR is less than 25, preferably less than 20, particularly  
 15 preferably less than 15, e.g. in the range from 0 to 14 or 0.1 to 13. This also means that  
 the degree of condensation of the silica in the support used is particularly high.

The identification of the  $Q_n$  structures ( $n = 2, 3, 4$ ) and the determination of the  
 percentage ratio is carried out by means of solid-state  $^{29}\text{Si}$ -NMR.

20  $Q_n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$  where  $n = 1, 2, 3$  or 4.

$Q_n$  is found at -110.8 ppm when  $n = 4$ , at -100.5 ppm when  $n = 3$  and at -90.7 ppm  
 when  $n = 2$  (standard: tetramethylsilane) ( $Q_0$  and  $Q_1$  were not identified). The analysis  
 25 is carried out under the conditions of "magic angle spinning" at room temperature  
 (20°C) (MAS 5500 Hz) with circular polarization (CP 5 ms) and using dipolar  
 decoupling of  $^1\text{H}$ . Owing to the partial superimposition of the signals, the intensities  
 were evaluated via line shape analysis. The line shape analysis was carried out using a  
 standard software package from Galactic Industries, with an iterative "least square fit"  
 30 being calculated.

The support material preferably contains no more than 1% by weight, in particular not  
 more than 0.5% by weight and particularly preferably < 500 ppm by weight, of  
 aluminum oxide, calculated as  $\text{Al}_2\text{O}_3$ .

35 Since the condensation of the silica can also be influenced by aluminum and iron, the  
 total concentration of  $\text{Al(III)}$  and  $\text{Fe(II and/or III)}$  is preferably less than 300 ppm,  
 particularly preferably less than 200 ppm, e.g. in the range from 0 to 180 ppm.

The alkali metal oxide content preferably results from the production of the support material and can be up to 2% by weight. It is frequently less than 1% by weight. Supports which are free of alkali metal oxide (from 0 to < 0.1% by weight) are also suitable. The proportion of MgO, CaO, TiO<sub>2</sub> or ZrO<sub>2</sub> can amount to up to 10% by weight of the support material and is preferably not more than 5% by weight. However, support materials which contain no detectable amounts of these metal oxides (from 0 to < 0.1% by weight) are also suitable.

Since Al(III) and Fe(II and/or III) incorporated in silica can produce acid centers, it is preferred that charge-compensating cations, preferably alkaline earth metal cations (M<sup>2+</sup>, M = Be, Mg, Ca, Sr, Ba), are present in the support. This means that the weight ratio of M(II) to (Al(III) + Fe(II and/or III)) is greater than 0.5, preferably >1, particularly preferably greater than 3.  
(M(II) = alkaline earth metal in the oxidation state 2).

Possible support materials are basically amorphous silicon dioxides comprising at least 90% by weight of silicon dioxide, with the remaining 10% by weight, preferably not more than 5% by weight, of the support material also being able to be another oxidic material, e.g. MgO, CaO, TiO<sub>2</sub>, ZrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and/or an alkali metal oxide.

In a preferred embodiment of the invention, the support material is halogen-free, in particular chlorine-free, i.e. the halogen content of the support material is less than 500 ppm by weight, e.g. in the range from 0 to 400 ppm by weight.

Preference is given to support materials which have a specific surface area in the range from 30 to 700 m<sup>2</sup>/g, preferably from 30 to 450 m<sup>2</sup>/g (BET surface area in accordance with DIN 66131).

Suitable amorphous support materials based on silicon dioxide are well known to those skilled in the art and are commercially available (cf., for example, O.W. Flörke, "Silica" in Ullmann's Encyclopedia of Industrial Chemistry 6th Edition on CD-ROM). They can either be of natural origin or have been produced synthetically. Examples of suitable amorphous support materials based on silicon dioxide are silica gels and pyrogenic silica. In a preferred embodiment of the invention, the catalysts have silica gels as support materials.

Depending on the way in which the invention is carried out, the support material can have various forms. If the process is carried out as a suspension process, the support material will usually be used in the form of finely divided powder for producing the catalysts of the invention. The powder preferably has particle sizes in the range from 1 to 200 µm, in particular from 1 to 100 µm. When the catalyst is used in fixed beds, it is usual to employ shaped bodies made of the support material which are obtainable, for

example, by extrusion, ram extrusion or tableting and can have, for example, the shape of spheres, pellets, cylinders, extrudates, rings or hollow cylinders, stars and the like. The dimensions of these shaped bodies are usually in the range from 1 mm to 25 mm. Catalyst extrudates having extrudate diameters of from 1.5 to 5 mm and extrudate  
5 lengths of from 2 to 25 mm are frequently used.

The ruthenium content in the catalysts can be varied over a wide range. It will preferably be at least 0.1% by weight, more preferably at least 0.2% by weight, and will frequently not exceed a value of 10% by weight, in each case based on the weight of  
10 the support material and calculated as elemental ruthenium. The ruthenium content is preferably in the range from 0.2 to 7% by weight, in particular in the range from 0.4 to 5% by weight, e.g. from 1.5 to 2% by weight.

The ruthenium catalysts used in the process of the invention are preferably produced  
15 by firstly treating the support material with a solution of a low molecular weight ruthenium compound, hereinafter referred to as (ruthenium) precursor, in such a way that the desired amount of ruthenium is taken up by the support material. Preferred solvents here are glacial acetic acid, water or mixtures thereof. This step will hereinafter also be referred to as impregnation. The support which has been treated in  
20 this way is subsequently dried, preferably with the upper limit to the temperature mentioned below being adhered to. If appropriate, the solid obtained in this way is then treated again with the aqueous solution of the ruthenium precursor and dried again. This procedure is repeated until the amount of ruthenium compound taken up by the support material corresponds to the desired ruthenium content of the catalyst.

25 The treatment or impregnation of the support material can be carried out in various ways and depends in a known manner on the shape of the support material. For example, the support material can be sprayed or flushed with the precursor solution or the support material can be suspended in the precursor solution. For example, the  
30 support material can be suspended in the aqueous solution of the ruthenium precursor and filtered off from the aqueous supernatant liquid after a particular time. The ruthenium content of the catalyst can then be controlled in a simple fashion via the amount of liquid taken up and the ruthenium concentration of the solution. The impregnation of the support material can, for example, also be carried out by treating  
35 the support with a defined amount of the solution of the ruthenium precursor corresponding to the maximum amount of liquid which can be taken up by the support material. For this purpose, the support material can, for example, be sprayed with the required amount of liquid. Suitable apparatuses for this purpose are the apparatuses customarily used for mixing liquids with solids (cf. Vauck/Müller, Grundoperationen  
40 chemischer Verfahrenstechnik, 10<sup>th</sup> edition, Deutscher Verlag für Grundstoffindustrie, 1994, p. 405 ff.), for example tumble dryers, impregnation drums, drum mixers, blade

mixers and the like. Monolithic supports are usually flushed with the aqueous solutions of the ruthenium precursor.

5 The solutions used for impregnation are preferably low in halogen, in particular low in chlorine, i.e. they comprise no halogen or less than 500 ppm by weight, in particular less than 100 ppm by weight, of halogen, e.g. from 0 to < 80 ppm by weight of halogen, based on the total weight of the solution. Ruthenium precursors used are therefore  $\text{RuCl}_3$  and preferably ruthenium compounds which comprise no chemically bound halogen and are sufficiently soluble in the solvent. These include, for example,  
10 ruthenium(III) nitrosyl nitrate ( $\text{Ru}(\text{NO})(\text{NO}_3)_3$ ), ruthenium(III) acetate and also alkali metal ruthenates(IV), e.g. sodium and potassium ruthenate(IV).

A very particularly preferred Ru precursor is Ru(III) acetate. This Ru compound is usually employed as a solution in acetic acid or glacial acetic acid, but it can also be  
15 used as a solid. The catalyst of the invention can be produced without using water.

Many ruthenium precursors are commercially available as solutions, but the corresponding solids can also be used. These precursors can be dissolved or diluted using the same component as the solvent supplied, e.g. nitric acid, acetic acid,  
20 hydrochloric acid, or preferably using water. Mixtures of water or solvent containing up to 50% by volume of one or more organic solvents which are miscible with water or solvents, e.g. mixtures with  $\text{C}_1$ - $\text{C}_4$ -alkanols such as methanol, ethanol, n-propanol or isopropanol, can also be used. All mixtures should be chosen so that a single solution or phase is present. The concentration of the ruthenium precursor in the solutions  
25 naturally depends on the amount of ruthenium precursor to be applied and on the uptake capacity of the support material for the solution and is preferably in the range from 0.1 to 20% by weight.

Drying can be carried out by the customary methods of solids drying with the upper  
30 limits to the temperature mentioned below being adhered to. Adherence to the upper limit to the drying temperature is important for the quality, i.e. the activity, of the catalyst. Exceeding the abovementioned drying temperatures leads to a significant loss in activity. Calcination of the support at higher temperatures, e.g. above  $300^\circ\text{C}$  or even  $400^\circ\text{C}$ , as is proposed in the prior art, is not only superfluous but also has an adverse  
35 effect on the activity of the catalyst. To achieve satisfactory drying rates, drying is preferably carried out at elevated temperature, preferably at  $\leq 180^\circ\text{C}$ , particularly preferably at  $\leq 160^\circ\text{C}$ , and at at least  $40^\circ\text{C}$ , in particular at least  $70^\circ\text{C}$ , especially at least  $100^\circ\text{C}$ , very particularly preferably at least  $140^\circ\text{C}$ .

40 Drying of the solid impregnated with the ruthenium precursor is usually carried out under atmospheric pressure, although a reduced pressure can also be employed to



promote drying. A gas stream, e.g. air or nitrogen, will frequently be passed over or through the material to be dried in order to promote drying.

5 The drying time naturally depends on the desired degree of drying and on the drying temperature and is preferably in the range from 1 hour to 30 hours, more preferably in the range from 2 to 10 hours.

10 Drying of the treated support material is preferably carried out to the point where the content of water or of volatile solvent constituents prior to the subsequent reduction is less than 5% by weight, in particular not more than 2% by weight, based on the total weight of the solid. The proportions by weight indicated correspond to the weight loss of the solid determined at a temperature of 160°C, a pressure of 1 bar and a time of 10 minutes. In this way, the activity of the catalysts used according to the invention can be increased further.

15 Drying is preferably carried out with the solid which has been treated with the precursor solution being kept in motion, for example by drying the solid in a rotary tube oven or a rotary sphere oven. In this way, the activity of the catalysts of the invention can be increased further.

20 The conversion of the solid obtained after drying into its catalytically active form is achieved by reducing the solid in a manner known per se at the temperatures indicated above.

25 For this purpose, the support material is brought into contact with hydrogen or a mixture of hydrogen and an inert gas at the temperatures indicated above. The absolute hydrogen pressure is of minor importance for the result of the reduction and will, for example, be in the range from 0.2 bar to 1.5 bar. The hydrogenation of the catalyst material is frequently carried out at a hydrogen pressure of one atmosphere in  
30 a stream of hydrogen. The reduction is preferably carried out with the solid being kept in motion, for example by reducing the solid in a rotary tube oven or a rotary sphere oven. In this way, the activity of the catalysts of the invention can be increased further.

35 The reduction can also be carried out by means of organic reducing agents such as hydrazine, formaldehyde, formates or acetates.

After the reduction, the catalyst can be passivated in a known manner, e.g. by briefly treating the catalyst with an oxygen-containing gas, e.g. air, but preferably with an inert gas mixture comprising from 1 to 10% by volume of oxygen, to improve the  
40 handleability. CO<sub>2</sub> or CO<sub>2</sub>/O<sub>2</sub> mixtures can also be employed here.

The active catalyst can also be stored under an inert organic solvent, e.g. ethylene glycol.

As a result of the way in which the catalysts of the invention are produced, the ruthenium is present as metallic ruthenium in these catalysts. Furthermore, electron-microscopic studies (SEM or TEM) have shown that a surface-impregnated catalyst is obtained: the ruthenium concentration within a catalyst particle decreases from the outside toward the interior, with a ruthenium layer being present at the surface of the particle. In the surface zone, crystalline ruthenium can be detected in the outer layer by means of SAD (selected area diffraction) and XRD (X-ray diffraction).

In addition, as a result of the use of halogen-free, in particular chlorine-free, ruthenium precursors and solvents in the production of the catalysts of the invention, their halide content, in particular chloride content, is below 0.05% by weight (0 to < 500 ppm by weight, e.g. in the range from 0-400 ppm by weight), based on the total weight of the catalyst.

The chloride content is, for example, determined by ion chromatography using the method described below.

In this document, all ppm figures are by weight (ppm by weight) unless indicated otherwise.

Preferred aromatic bisglycidyl ethers of the formula II have a content of chloride and/or organically bound chlorine of  $\leq 1000$  ppm by weight, in particular < 950 ppm by weight, particularly preferably in the range from 0 to < 800 ppm by weight, e.g. from 600 to 1000 ppm by weight.

The content of chloride and/or organically bound chlorine is, for example, determined by ion chromatography or coulometrically using the methods described below.

According to a particular embodiment of the process according to the invention, it has been recognized that it is, surprisingly, also advantageous for the aromatic bisglycidyl ether of the formula II which is used to have a content of corresponding oligomeric bisglycidyl ethers of less than 10% by weight, in particular less than 5% by weight, particularly preferably less than 1.5% by weight, very particularly preferably less than 0.5% by weight, e.g. in the range from 0 to < 0.4% by weight.

It has been found that the oligomer content of the feed has a critical influence on the operating life of the catalyst, i.e. the conversion remains at a high level for longer. When a bisglycidyl ether II which has, for example, been distilled and is therefore low in oligomers is used, a dramatically slowed catalyst deactivation compared to a

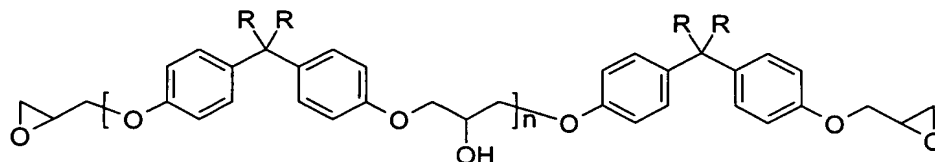
corresponding commercial standard product (e.g.: ARALDIT GY 240 BD from Vantico) is observed.

5 The oligomer content of the aromatic bisglycidyl ether of the formula II which is used is preferably determined by GPC (gel permeation chromatography) or by determination of the evaporation residue.

10 The evaporation residue is determined by heating the aromatic bisglycidyl ether at 200°C for 2 hours and at 300°C for a further 2 hours, in each case at 3 mbar.

For the further respective conditions for determining the oligomer content, see below.

15 The respective oligomeric bisglycidyl ethers generally have a molecular weight determined by GPC in the range from 380 to 1500 g/mol and possess, for example, the following structures (cf., for example, Journal of Chromatography 238 (1982), pages 385-398, page 387):



20  $\text{R} = \text{CH}_3$  or  $\text{H}$ .  $n = 1, 2, 3$  or  $4$ .

25 The respective oligomeric bisglycidyl ethers have a molecular weight in the range from 568 to 1338 g/mol, in particular from 568 to 812 g/mol, when  $\text{R} = \text{H}$  and have a molecular weight in the range from 624 to 1478 g/mol, in particular from 624 to 908 g/mol, when  $\text{R} = \text{CH}_3$ .

30 The removal of the oligomers is carried out, for example, by means of chromatography or, on a relatively large scale, preferably by distillation, e.g. in a batch distillation on the laboratory scale or in a thin film evaporator, preferably in a short path distillation, on an industrial scale, in each case under reduced pressure.

In a batch distillation for the removal of oligomers at, for example, a pressure of about 2 mbar, the bath temperature is about 260°C and the temperature at which the distillate goes over at the top is about 229°C.

35 Oligomer removal can likewise be carried out under milder conditions, for example under reduced pressures in the range from 1 to  $10^{-3}$  mbar. At a working pressure of 0.1 mbar, the boiling point of the oligomer-comprising starting material is reduced by 20-30°C, depending on the starting material, and the thermal stress on the product is

therefore also reduced. To minimize the thermal stress, the distillation is preferably carried out continuously in a thin film evaporation or particularly preferably in a short path evaporation.

- 5 In the process of the invention, the hydrogenation of the compounds II preferably occurs in the liquid phase. Owing to the sometimes high viscosity of the compounds II, they are preferably used as a solution or mixture in an organic solvent.

- Possible organic solvents are basically those which are able to dissolve the compound  
10 II virtually completely or are completely miscible with this and are inert under the hydrogenation conditions, i.e. are not hydrogenated.

- Examples of suitable solvents are cyclic and alicyclic ethers, e.g. tetrahydrofuran, dioxane, methyl tert-butyl ether, dimethoxyethane, dimethoxypropane, dimethyl  
15 diethylene glycol, aliphatic alcohols such as methanol, ethanol, n-propanol or isopropanol, n-, 2-, iso- or tert-butanol, carboxylic esters such as methyl acetate, ethyl acetate, propyl acetate or butyl acetate, and also aliphatic ether alcohols such as methoxypropanol.

- 20 The concentration of compound II in the liquid phase to be hydrogenated can in principle be chosen freely and is frequently in the range from 20 to 95% by weight, based on the total weight of the solution/mixture. In the case of compounds II which are sufficiently fluid under the reaction conditions, the hydrogenation can also be carried out in the absence of a solvent.

- 25 As an alternative to carrying out the reaction (hydrogenation) under anhydrous conditions, in a number of cases, it has been found to be useful to carry out the reaction (hydrogenation) in the presence of water. The proportion of water can be, based on the mixture to be hydrogenated, up to 10% by weight, e.g. from 0.1 to 10%  
30 by weight, preferably from 0.2 to 7% by weight and in particular from 0.5 to 5% by weight.

- The actual hydrogenation is usually carried out by a method analogous to the known hydrogenation processes for the preparation of compounds I, as are described in the  
35 prior art mentioned at the outset. For this purpose, the compound II, preferably as a liquid phase, is brought into contact with the catalyst in the presence of hydrogen. The catalyst can either be suspended in the liquid phase (suspension process) or the liquid phase is passed over a moving bed of catalyst (moving-bed process) or a fixed bed of catalyst (fixed-bed process). The hydrogenation can be carried out either continuously  
40 or batchwise. The process of the invention is preferably carried out as a fixed-bed process in trickle-bed reactors. The hydrogen can be passed over the catalyst either in

cocurrent with or in countercurrent to the solution of the starting material to be hydrogenated.

Suitable apparatuses for carrying out a hydrogenation in the suspension mode and also for hydrogenation over a moving bed of catalyst or a fixed bed of catalyst are

- 5 known from the prior art, e.g. from Ullmanns Enzyklopädie der Technischen Chemie, 4<sup>th</sup> edition, Volume 13, p. 135 ff. and also from P. N. Rylander, "Hydrogenation and Dehydrogenation" in Ullmann's Encyclopedia of Industrial Chemistry, 5th ed. on CD-ROM.

- 10 The hydrogenation can be carried out either at a hydrogen pressure of one atmosphere or at a superatmospheric pressure of hydrogen, e.g. an absolute hydrogen pressure of at least 1.1 bar, preferably at least 10 bar. In general, the absolute hydrogen pressure will not exceed 325 bar and preferably 300 bar. The absolute hydrogen pressure is particularly preferably in the range from 50 to 300 bar.

- 15 The reaction temperatures are generally at least 30°C and will frequently not exceed a value of 150°C. In particular, the hydrogenation process is carried out at temperatures in the range from 40 to 100°C, and particularly preferably in the range from 45 to 80°C.

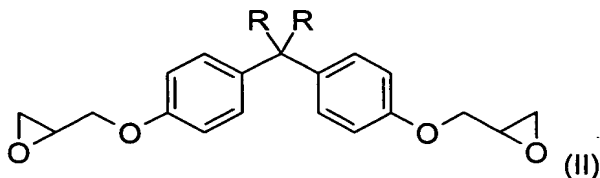
- 20 Possible reaction gases are hydrogen and also hydrogen-containing gases which comprise no catalyst poisons such as carbon monoxide or sulfur-containing gases, e.g. mixtures of hydrogen with inert gases such as nitrogen or offgases from a reformer, which usually further comprise volatile hydrocarbons. Preference is given to using pure hydrogen (purity  $\geq 99.9\%$  by volume, in particular  $\geq 99.95\%$  by volume, particularly  
25 preferably  $\geq 99.99\%$  by volume).

- Owing to the high catalyst activity, comparatively small amounts of catalyst, based on the starting material used, are required. Thus, less than 5 mol%, e.g. from 0.2 mol% to 2 mol%, of ruthenium will preferably be used per 1 mol of compound II in a suspension  
30 process carried out batchwise. When the hydrogenation is carried out continuously, the starting material II to be hydrogenated will usually be passed over the catalyst in an amount of from 0.05 to 3 kg/(l(catalyst) • h), in particular from 0.15 to 2 kg/(l(catalyst) • h).

- Of course, when the activity of the catalysts used in this process drops, they can be  
35 regenerated by the customary methods known to those skilled in the art for noble metal catalysts such as ruthenium catalysts. Mention may here be made of, for example, treatment of the catalyst with oxygen as described in BE 882 279, treatment with dilute, halogen-free mineral acids as described in US 4,072,628, or treatment with hydrogen peroxide, e.g. in the form of aqueous solutions having a concentration of from 0.1 to  
40 35% by weight, or treatment with other oxidizing substances, preferably in the form of halogen-free solutions. The catalyst is usually rinsed with a solvent, e.g. water, after the reactivation and before renewed use.

The hydrogenation process of the invention preferably comprises the complete hydrogenation of the aromatic rings of the bisglycidyl ether of the formula II

5



used, where R is CH<sub>3</sub> or H, with the degree of hydrogenation being > 98%, particularly preferably > 98.5%, very particularly preferably > 99%, e.g. > 99.3%, in particular > 99.5%, e.g. in the range from > 99.8 to 100%.

10

The degree of hydrogenation (Q) is defined by

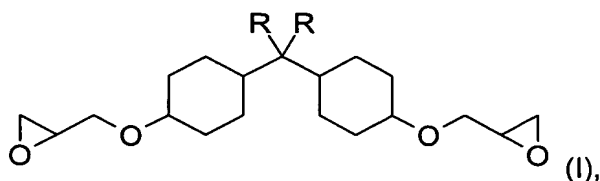
$Q (\%) = ([\text{number of cycloaliphatic C6 rings in the product}] / [\text{number of aromatic C6 rings in the starting material}]) \cdot 100$

15

The ratio, e.g. molar ratio, of the aliphatic and aromatic C6 rings can preferably be determined by means of <sup>1</sup>H-NMR spectroscopy (integration of the aromatic and correspondingly cycloaliphatic <sup>1</sup>H signals).

20

The invention likewise provides bisglycidyl ethers of the formula I

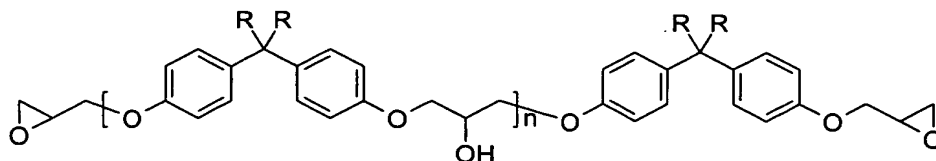


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where R is CH<sub>3</sub> or H, which can be prepared by the hydrogenation process of the invention.

The bisglycidyl ethers of the formula I preferably have a content of corresponding oligomeric ring-hydrogenated bisglycidyl ethers of the formula

30



(where R is CH<sub>3</sub> or H) in which n = 1, 2, 3 or 4, of less than 10% by weight, particularly preferably less than 5% by weight, in particular less than 1.5% by weight, very particularly preferably less than 0.5% by weight, e.g. in the range from 0 to < 0.4% by weight.

5

The content of oligomeric ring-hydrogenated bisglycidyl ethers is preferably determined by heating the aromatic bisglycidyl ether for 2 hours at 200°C and for a further 2 hours at 300°C, in each case at 3 mbar, or by GPC measurement (gel permeation chromatography).

10

As regards the further conditions for determining the oligomer content, see below.

The bisglycidyl ethers of the formula I preferably have a total chlorine content determined in accordance with DIN 51408 of less than 1000 ppm by weight, in particular less than 800 ppm by weight, very particularly preferably less than 600 ppm by weight, e.g. in the range from 0 to 400 ppm by weight.

15

The bisglycidyl ethers of the formula I preferably have a ruthenium content determined by mass spectrometry combined with inductively coupled plasma (ICP-MS) of less than 0.3 ppm by weight, in particular less than 0.2 ppm by weight, very particularly preferably less than 0.1 ppm by weight, e.g. in the range from 0 to 0.09 ppm by weight.

20

The bisglycidyl ethers of the formula I preferably have a platinum-cobalt color number (APHA color number) determined in accordance with DIN ISO 6271 of less than 30, particularly preferably less than 25, very particularly preferably less than 20, e.g. in the range from 0 to 18.

25

The bisglycidyl ethers of the formula I preferably have an epoxy equivalent weight determined in accordance with the standard ASTM-D-1652-88 in the range from 170 to 240 g/equivalent, particularly preferably in the range from 175 to 225 g/equivalent, very particularly preferably in the range from 180 to 220 g/equivalent.

30

The bisglycidyl ethers of the formula I preferably have a proportion of hydrolyzable chlorine determined in accordance with DIN 53188 of less than 500 ppm by weight, particularly preferably less than 400 ppm by weight, very particularly preferably less than 350 ppm by weight, e.g. in the range from 0 to 300 ppm by weight.

35

The bisglycidyl ethers of the formula I preferably have a kinematic viscosity determined in accordance with DIN 51562 of less than 800 mm<sup>2</sup>/s, particularly preferably less than 700 mm<sup>2</sup>/s, very particularly preferably less than 650 mm<sup>2</sup>/s, e.g. in the range from 400 to 630 mm<sup>2</sup>/s, in each case at 25°C.

40

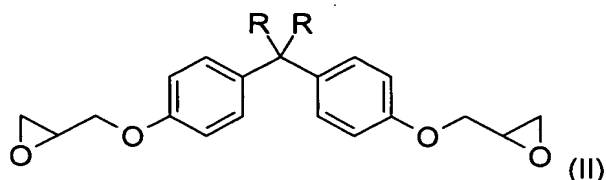
The bisglycidyl ethers of the formula I preferably have a cis-cis:cis-trans:trans-trans isomer ratio in the range 44-63%:34-53%:3-22%.

The cis-cis:cis-trans:trans-trans isomer ratio is particularly preferably in the range 46-60%:36-50%:4-18%.

- 5 The cis-cis:cis-trans:trans-trans isomer ratio is very particularly preferably in the range 48-57%:38-47%:5-14%.

In particular, the cis-cis:cis-trans:trans-trans isomer ratio is in the range 51-56%:39-44%:5-10%.

- 10 The bisglycidyl ethers of the formula I are particularly preferably obtained by complete hydrogenation of the aromatic rings of a bisglycidyl ether of the formula II



- 15 where R is CH<sub>3</sub> or H, with the degree of hydrogenation being > 98%, particularly preferably > 98.5%, very particularly preferably > 99%, e.g. > 99.3%, in particular > 99.5%, e.g. in the range from > 99.8 to 100%.

#### Examples

20

##### 1. Production of catalysts according to the invention

A defined amount of the support material was placed in a dish and impregnated with 90-95% of the maximum amount of a solution of Ru(III) acetate (about 5% Ru in 100% acetic acid) in water which can be taken up by the support material. The following supports were selected:

25

C15 from Grace (BET surface area = 181 m<sup>2</sup>/g, pore volume of 1.1 ml/g, Q<sub>2</sub>/Q<sub>3</sub> = 13%, M(II) : (Al(III) + Fe(II and/or III)) = 7.0), (M(II) = Ca(II) + Mg(II)), and

30

Davicat® S557 (Grade 57) from Grace-Davison (BET surface area = 340 m<sup>2</sup>/g, pore volume of 1.1 ml/g, Q<sub>2</sub>/Q<sub>3</sub> = 8.8%, M(II) : (Al(III) + Fe(II and/or III)) = 4.6), (M(II) = Ca(II) + Mg(II)).

- 35 The material obtained in this way was in each case dried overnight at 120°C. The dried material was reduced for 2 hours at 300°C in a stream of hydrogen at atmospheric pressure in a rotary sphere oven. After cooling and making the system inert (N<sub>2</sub>), the catalyst was passivated with dilute air at room temperature. The reduced and



passivated catalyst contained about 1.6 – 2% by weight of Ru, based on the total mass of the catalyst obtained.

TEM analysis:

- 5 The ruthenium concentration within a catalyst particle of the catalyst of the invention decreases from the outside toward the interior, with an Ru layer having a thickness of up to about 200 nm being located at the particle surface. In the interior of the catalyst particle, the Ru particles have a size of up to about 2 nm. Beneath the ruthenium shell, aggregated and/or agglomerated Ru particles are observed in places. In this region, 10 the size of the individual Ru particles is up to about 4 nm. Crystalline ruthenium is detected in the shell by means of SAD.

XRD analysis indicates a ruthenium crystallite size of about 8 nm.

- 15 The pore volume was determined by means of nitrogen sorption in accordance with DIN 66131.

The identification of the  $Q_n$  structures ( $n = 2, 3, 4$ ) and the determination of the percentage ratio were carried out by means of solid-state  $^{29}\text{Si}$ -NMR.

- 20  $Q_n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$  where  $n = 1, 2, 3$  or  $4$ .  
 $Q_n$  is found at -110.8 ppm when  $n = 4$ , at -100.5 ppm when  $n = 3$  and at -90.7 ppm when  $n = 2$  (standard: tetramethylsilane) ( $Q_0$  and  $Q_1$  were not identified). The analysis was carried out under the conditions of "magic angle spinning" at room temperature (20°C) (MAS 5500 Hz) with circular polarization (CP 5 ms) and using dipolar 25 decoupling of  $^1\text{H}$ . Owing to the partial superimposition of the signals, the intensities were determined by line shape analysis. The line shape analysis was carried out using a standard software package from Galactic Industries, with an iterative "least squares fit" being calculated.

- 30 Tabular overview:

	Catalyst B from WO-A-02/100538 (3 mm extrudates)	Catalyst based on Davicat® S557 = catalyst C (according to the invention)	Catalyst based on C15 (Grace) = catalyst D (according to the invention)
N <sub>2</sub> sorption:			
BET, m <sup>2</sup> /g	117	341	181
Pore diameter, nm	24	11	19
Pore volume, ml/g	0.69	1.15	1.1
Fe + Al, ppm *)	400	125	47
(Ca+Mg) : (Fe+Al),	0.1	4.6	7.0

ppm/ppm \*)

<sup>29</sup> Si-NMR (MAS)	30	9	13
Q <sub>2</sub> /Q <sub>3</sub> , %			

\*) Oxidation states: Fe(II and/or III), Al(III), Ca(II), Mg(II).

5 The support of catalyst A from WO 02/100 538 corresponds to the support of catalyst B from WO 02/100 538 (same chemical composition), but the BET surface area is 68 m<sup>2</sup>/g and the pore volume is 0.8 ml/g.

## 2. Description of the experimental apparatus and hydrogenation examples

10 Reactors used were heated reaction tubes made of stainless steel (reactor 1: length 0.8 m; diameter = 12 mm; or reactor 2: length = 1.4 m, diameter = 12 mm) which were charged with catalyst and were provided with a circulation pump for the starting material and a separator with level control for sampling and regulation of the offgas. The reactors could be operated with and without circulation, as desired.

15 The conversion and the degree of hydrogenation were determined by means of <sup>1</sup>H-NMR:  
sample quantity: 20-40 mg, solvent: CDCl<sub>3</sub>, 700  $\mu$ liters using TMS as reference signal,  
sample tube: 5 mm diameter, 400 or 500 MHz, 20°C; decrease in the signals of the  
20 aromatic protons versus increase in the signals of aliphatic protons. The conversion reported in the examples is based on the hydrogenation of the aromatic groups.

The decrease in the epoxide groups was determined by comparison of the epoxide equivalent (EEW) before and after hydrogenation, in each case determined in  
25 accordance with the standard ASTM-D-1652-88.

The determination of ruthenium in the output which had been freed of THF and water was carried out by mass spectrometry combined with inductively coupled plasma (ICP-MS, see below).

30 Hydrogenation example 1 (comparative example)

In the above-described experimental apparatus 1 (reactor charged with 75 ml of catalyst D according to the invention), a 20% strength by weight solution of 2,2-di[p-glycidoxyphenyl]propane (standard commercial product, e.g. ARALDIT GY 240 BD  
35 from Vantico, EEW = 182) in THF, which comprised 3% by weight of water, was

hydrogenated at a temperature of 50°C and a hydrogen pressure of 250 bar for a period of 72 hours. The reactor was operated in the upflow mode.

At a space velocity over the catalyst of 0.15 kg/l<sub>cat.</sub> • h, the conversion decreased from 91% (EEW = 217, selectivity: 86%) at the beginning to 40% (EEW = 192, selectivity: 96%) after 72 hours.

The ruthenium content in the output (which had been freed of the solvent) was < 1 ppm.

#### 10 Hydrogenation example 2

In the above-described experimental apparatus 1 (reactor charged with 75 ml of catalyst D according to the invention), initially a 20% strength by weight solution and then after 224 hours of operation a 30% strength by weight solution of 2,2-di[p-glycidoxyphenyl]propane (distilled product, EEW = 172) in THF, which each comprised 3% by weight of water, was hydrogenated at a temperature of 50°C and a hydrogen pressure of 250 bar. The reactor was operated in the upflow mode.

At a space velocity over the catalyst of 0.15 kg/l<sub>cat.</sub> • h, the conversion during the first 224 hours was 90% (EEW = 197, selectivity: 88%).

After changing over to the 30% strength by weight solution, the conversion rose to 96% (EEW = 205, selectivity: 86%). After 464 hours of operation, a decrease in conversion to 94% (EEW = 199, selectivity: 89%) was observed.

The Ru content in the output (which had been freed of the solvent) was < 1 ppm.

#### 25 Hydrogenation example 3

In the above-described experimental apparatus 2 (reactor charged with 120 ml of catalyst D according to the invention), a 30% strength by weight solution initially and then after 437 hours of operation a 40% strength by weight solution of 2,2-di[p-glycidoxyphenyl]propane (distilled product, EEW = 172) in THF, which each comprised 3-6% by weight of water, was hydrogenated at a temperature of 50-55°C and a hydrogen pressure of 250 bar. The reactor was operated in the downflow mode.

At a space velocity over the catalyst of 0.15 kg/l<sub>cat.</sub> • h and a feed/circulation ratio of 60, the conversion after 437 hours was 82% (EEW = 191, selectivity: 93%).

After changing over to the 40% strength by weight solution, conversion and selectivity remained constant. After 1325 hours of operation, no decrease in conversion was observed (conversion: 83%, EEW = 191, selectivity: 93%).

The ruthenium content in the output (which had been freed of the solvent) was < 0.1 ppm.

## Hydrogenation example 4

In the above-described experimental apparatus 2 (reactor charged with 75 ml of catalyst D according to the invention), a partially reacted product prepared as described in example 3 was subjected to an after-hydrogenation to achieve the desired final conversion. The reactor was operated in the upflow mode (upflow mode operation).

The 40% strength by weight solution used had been reacted to a conversion of 84% at a selectivity of 91% (EEW = 196) and was after-hydrogenated at 250 bar and 55°C. The final product was reacted to a conversion of 98.6% (EEW = 209; selectivity: 85%). The ruthenium content in the (output which had been freed of the solvent) was < 0.1 ppm.

The stereoisomer ratio of the product obtained (2,2'-[1-methyleneethylidene]bis(4,1-cyclohexanediylloxymethylene)]bisoxirane) was found (by GC, NMR, cf. below) to be: 52% cis-cis : 42% trans-cis : 6% trans-trans

## Hydrogenation example 5

21 g of the catalyst (catalyst D, Ru content: 1.7% by weight) were placed in a catalyst basket in a 1.2 liter pressure autoclave provided with a sparging stirrer (700 rpm) and sampling tube and heated with 600 g of a 40% strength by weight solution of low-oligomer bisphenol A bisglycidyl ether (distilled product, EEW = 171 g/eq.) in THF comprising 4.5% by weight of water to 50°C and the bisglycidyl ether was hydrogenated at a hydrogen pressure of 250 bar. After a reaction time of 24 hours, the autoclave was cooled to room temperature and depressurized, the reaction mixture was drained. Fine material which had been abraded mechanically from the catalyst was separated off by means of a filter. An aliquot of the colorless reaction product mixture was analyzed after removal of the solvent on a rotary evaporator (conditions: oil bath temperature: 130°C, vacuum: 5-10 mbar, 15 minutes): Ru content of the reaction product mixture: < 0.1 ppm conversion according to <sup>1</sup>H-NMR: > 99% EEW = 207 g/eq.

The stereoisomer ratio of the product obtained (2,2'-[1-methylethylidene]bis(4,1-cyclohexanediylloxymethylene)]bisoxirane) was determined (by GC, NMR) as:

cis-cis (%)	= 53
cis-trans (%)	= 41
trans-trans (%)	= 6

## Hydrogenation example 6

- 21 g of the catalyst (catalyst D, Ru content: 2.0% by weight) were placed in a catalyst basket in a 1.2 liter pressure autoclave provided with a sparging stirrer (700 rpm) and sampling tube and heated with 600 g of a 40% strength by weight solution of low-oligomer bisphenol A bisglycidyl ether (distilled product, EEW = 171 g/eq.) in THF comprising 4.5% by weight of water to 50°C and the bisglycidyl ether was hydrogenated at a hydrogen pressure of 250 bar. After a reaction time of 11 hours, the conversion of the aromatic was complete according to <sup>1</sup>H-NMR. The autoclave was cooled to room temperature and depressurized, the reaction mixture was drained. Fine material which had been abraded mechanically from the catalyst was separated off by means of a filter. An aliquot of the colorless reaction product mixture was analyzed after removal of the solvent on a rotary evaporator (conditions: oil bath temperature: 130°C, vacuum: 5-10 mbar, 15 minutes):
- Ru content of the reaction product mixture: < 0.1 ppm  
EEW = 208 g/eq.  
conversion according to <sup>1</sup>H-NMR: > 99%
- The stereoisomer ratio of the product obtained (2,2'-[1-methylethylidene)bis(4,1-cyclohexanediylloxymethylene)]bisoxirane) was determined (by GC, NMR) as:
- |                 |      |
|-----------------|------|
| cis-cis (%)     | = 56 |
| cis-trans (%)   | = 39 |
| trans-trans (%) | = 5  |

## Hydrogenation example 7

- 17.9 g of the catalyst (catalyst D, Ru content: 2.0% by weight) were placed in a catalyst basket in a 1.2 liter pressure autoclave provided with a sparging stirrer (700 rpm) and sampling tube and heated with 600 g of a 40% strength by weight solution of low-oligomer bisphenol A bisglycidyl ether (distilled product, EEW = 171 g/eq.) in THF comprising 4.5% by weight of water to 50°C and the bisglycidyl ether was hydrogenated at a hydrogen pressure of 250 bar. After a reaction time of 14 hours, the conversion of the aromatic was complete according to <sup>1</sup>H-NMR. The autoclave was cooled to room temperature and depressurized, the reaction mixture was drained. Fine material which had been abraded mechanically from the catalyst was separated off by means of a filter. An aliquot of the colorless reaction product mixture was analyzed after removal of the solvent on a rotary evaporator (conditions: oil bath temperature: 130°C, vacuum: 5-10 mbar, 15 minutes):
- Ru content of the reaction product mixture: < 0.1 ppm  
EEW = 215 g/eq.  
conversion according to <sup>1</sup>H-NMR: > 99%
- The stereoisomer ratio of the product obtained (2,2'-[1-methylethylidene)bis(4,1-cyclohexanediylloxymethylene)]bisoxirane) was determined (by GC, NMR) as:

cis-cis (%) = 56  
 cis-trans (%) = 39  
 trans-trans (%) = 5

#### 5 Hydrogenation example 8

In a 1.2 liter pressure autoclave provided with a sparging stirrer (700 rpm) and sampling tube, 4.8 g of the catalyst (5% by weight Rh/activated carbon, from Aldrich, catalog No. 20,616-4, lot No. 90621001) were heated with 600 g of a 40% strength by weight solution of low-oligomer bisphenol A bisglycidyl ether (distilled product, EEW = 171 g/eq.) in THF comprising 4.5% by weight of water to 50°C and the bisglycidyl ether was hydrogenated at a hydrogen pressure of 250 bar. After a reaction time of 2 hours, the conversion of the aromatic was complete according to <sup>1</sup>H-NMR. The autoclave was cooled to room temperature and depressurized, the reaction mixture was drained. The mixture was filtered. An aliquot of the colorless reaction product mixture was analyzed after removal of the solvent on a rotary evaporator (conditions: oil bath temperature: 130°C, vacuum: 5-10 mbar, 15 minutes):

EEW = 260 g/eq.

conversion according to <sup>1</sup>H-NMR: > 99%

The stereoisomer ratio of the product obtained (2,2'-[1-methylethylidene]bis(4,1-cyclohexanedioxy)methylene)]bisoxirane) was determined (by GC, NMR) as:

cis-cis (%) = 57

cis-trans (%) = 38

trans-trans (%) = 5

In summary, the examples show that the oligomer content of the feed has a decisive influence on the operating life of the catalyst: when a distilled feed was used (example 2 – "low-oligomer" feed), a dramatically slowed catalyst deactivation compared to a commercial standard product (example 1 – "oligomer-rich feed") was observed. The oligomer content of the products used in the examples was determined by means of GPC measurement (gel permeation chromatography):

Product	"Monomer"	"Oligomers"	
	180 – <380 g/mol	380 – <520 g/mol	520 – 1500 g/mol
Standard product	89.98% by area	2.05% by area	7.97% by area
Distilled product	98.80% by area	0.93% by area	0.27% by area

Molecular weight of 2,2-di[p-glycidioxyphenyl]propane: 340 g/mol

## 3. Description of the GPC measurement conditions

Stationary phase: 5 styrene-divinylbenzene gel columns "PSS SDV linear M" (each 300 x 8 mm) from PSS GmbH (temperature: 35°C).

5 Mobile phase: THF (flow: 1.2 ml/min.).

Calibration: MW 500-10 000 000 g/mol using PS calibration kit from Polymer Laboratories. In the oligomer range: ethylbenzene / 1,3-diphenylbutane / 1,3,5-triphenylhexane / 1,3,5,7-tetraphenyloctane / 1,3,5,7,9-pentaphenyldecane.

Evaluation limit: 180 g/mol. Detection: RI (refractive index) Waters 410, UV (at 254 nm)

10 Spectra Series UV 100.

The molar masses reported are, owing to different hydrodynamic volumes of the individual polymer types in solution, relative values based on polystyrene as calibration substance and are thus not absolute values.

15

The oligomer content in % by area determined by GPC measurement can be converted into % by weight by means of an internal or external standard.

20

GPC analysis of an aromatic bisglycidyl ether of the formula II ( $R = CH_3$ ) used in the hydrogenation process of the invention displayed, for example, in addition to the monomer, the following contents of corresponding oligomeric bisglycidyl ethers:

Molar masses in the range 180 - < 380 g/mol: > 98.5% by area,

in the range 380 - < 520 g/mol: < 1.3% by area,

25 in the range 520 - < 860 g/mol: < 0.80% by area and

in the range 860 - 1500 g/mol: < 0.15% by area.

## 4. Description of the method for determining the evaporation residue

30

About 0.5 g of each sample was weighed into a weighing bottle. The weighing bottles were subsequently placed at room temperature in a plate-heated vacuum drying oven and the drying oven was evacuated. At a pressure of 3 mbar, the temperature was increased to 200°C and the sample was dried for 2 hours. The temperature was increased to 300°C for a further 2 hours, and the samples were subsequently cooled to room temperature in a desiccator and weighed.

35

+The residue (oligomer content) determined by this method on standard product (ARALDIT GY 240 BD from Vantico) was 6.1% by weight.

The residue (oligomer content) determined by this method on distilled standard product was 0% by weight. (Distillation conditions: 1 mbar, bath temperature 260°C, and temperature at which the distillate went over at the top 229°C).

5 5. Determination of the cis-cis:cis-trans:trans-trans isomer ratios

A hydrogenated bisphenol A bisglycidyl ether ( $R = CH_3$ ) product was analyzed by means of gas chromatography (GC and GC-MS). Here, 3 signals were identified as hydrogenated bisphenol A bisglycidyl ether.

- 10 A plurality of isomers can be formed by hydrogenation of the bisphenol A unit of the bisglycidyl ether. Depending on the arrangement of the substituents on the cyclohexane rings, cis-cis, trans-trans or cis-trans isomerism can occur. To identify the three isomers, the products of the respective peaks were collected preparatively by means of a column arrangement. Each fraction was subsequently
- 15 characterized by NMR spectroscopy ( $^1H$ ,  $^{13}C$ , TOCSY, HSQC).

The preparative GC was carried out using a GC system having a column arrangement. The sample was pre-separated on a Sil-5 capillary ( $l = 15\text{ m}$ ,  $ID = 0.53\text{ mm}$ ,  $df = 3\text{ }\mu\text{m}$ ). The signals were cut to a 2nd GC column with the aid of a DEANS connection. This

20 column served to check the quality of the preparative cut. Each peak was subsequently collected with the aid of a fraction collector. 28 injections of an about 10% strength by weight solution of the sample were prepared, corresponding to about 10  $\mu\text{g}$  of each component.

- Characterization of the isolated components was then carried out by NMR
- 25 spectroscopy.

The determination of the isomer ratios of a hydrogenated bisphenol F bisglycidyl ether ( $R = H$ ) was carried out analogously.

30 6. Determination of ruthenium in the ring-hydrogenated bisglycidyl ether of the formula I

The sample was diluted by a factor of 100 with a suitable organic solvent (e.g. NMP). The ruthenium content of this solution was determined by mass spectrometry

35 combined with inductively coupled plasma (ICP-MS).

Instrument: ICP-MS spectrometer, e.g. Agilent 7500s

Measurement conditions:

Calibration: external calibration in organic matrix

- 40 Atomizer: Meinhardt

Mass: Ru102



The calibration curve was chosen so that the required output value could be determined with certainty in the diluted measurement solution.

## 7. Determination of chloride and organically bound chlorine

5

The determination of chloride was carried out by ion chromatography.

Sample preparation:

About 1 g of the sample was dissolved in toluene and extracted with 10 ml of high-purity water.

10

The aqueous phase was measured by means of ion chromatography.

Measurement conditions:

Ion chromatography system: Metrohm

Precolumn: DIONEX AG 12

Separation column: DIONEX AS 12

15

Eluent: (2.7 mmol of Na<sub>2</sub>CO<sub>3</sub> + 0.28 mmol of NaHCO<sub>3</sub>)/liter of water

Flow: 1 ml/min.

Detection: conductivity after chemical suppression

Suppressor: Metrohm module 753

20

50 mmol of H<sub>2</sub>SO<sub>4</sub>; high-purity water  
(flow: about 0.4 ml/min.)

Calibration: 0.01 mg/l to 0.1 mg/l

25

Coulometric determination of organically bound chlorine (total chlorine) in accordance with DIN 51408, part 2, "Bestimmung des Chlorgehalts"

The sample was burnt at a temperature of about 1020°C in an oxygen atmosphere.

The bound chlorine in the sample was in this way converted into hydrogen chloride.

30

The nitrous gasses, sulfur oxide and water formed in the combustion are removed and the combustion gas which has been purified in this way is fed into the coulometer cell.

Here, the coulometric determination of the chloride formed is effected according to  $\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}$ .

Sample weight range: 1 to 50 mg

35

Determination limit: about 1 mg/kg (substance-dependent)

Instrument: Euroglas (LHG), "ECS-1200"

Reference: F. Ehrenberger, "Quantitative organische Elementaranalyse", ISBN 3-527-28056-1.